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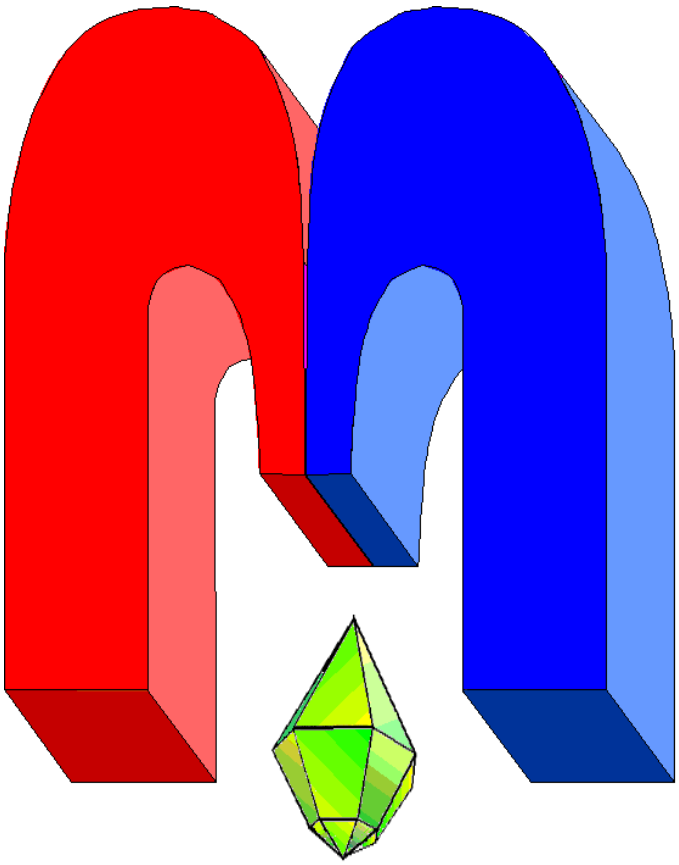

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Probing the Metal-to-Insulator Transition in $LaCu_3Ru_xTi_{4-x}O_{12}$ by Gd-ESR†

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$LaCu_3Ru_xTi_{4-x}O_{12}$ undergoes a metal-to-insulator transition (MIT) from a heavy-fermion metal ($x = 4$) with moderately enhanced electronic masses to an antiferromagnetic insulator ($x = 0$) with colossal dielectric constants. So far, the exact value x_c of the MIT could not be obtained from electrical resistivity or specific-heat data, which are governed by local-moment scattering and Schottky anomalies, respectively. To investigate the MIT by electron spin resonance (ESR) technique, polycrystalline samples of the solid-solution series $La_{1-y}Gd_yCu_3Ru_xTi_{4-x}O_{12}$ were synthesized for the substitution range $1 \leq x \leq 4$ and $0.05 \leq y \leq 0.15$, where Gd^{3+} ($^8S_{7/2}$ ground state) serves as ESR probe. For $x = 4$ the Gd^{3+} ESR linewidth exhibits an enhanced Korringa relaxation at low temperatures ($T < 50$ K) as typically expected for heavy-fermion metals. This metallic contribution gradually diminishes on decreasing Ru content x and vanishes for $x = 2.25$ localizing the MIT close to the onset of spin-glass behavior arising for $x \leq 2$.

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Keywords: heavy fermions, metal-to-insulator transition, electron spin resonance

1. Introduction

Originally heavy-fermion behavior was observed in intermetallic compounds containing elements with partially filled $4f$ or $5f$ shells, like Ce, Yb or U. Prominent examples are, e.g., $CeAl_3$, $CeCu_2Si_2$, $YbRh_2Si_2$, and UPt_3 [1–4]. Due to the Kondo effect, below a certain characteristic temperature T^* of the order of 10 K the local f moments become screened by the conduction electrons. In turn, these materials exhibit metallic properties with strongly enhanced effective masses $m^*/m_e \approx 1000$ with respect to the free electron mass m_e resulting in a correspondingly strong enhancement of the Sommerfeld coefficient of the specific heat as well as of the Pauli susceptibility. Later on, also several d-electron derived heavy-fermion compounds have been discovered in the large manifold of transition-metal oxides, like the magnetically frustrated spinel LiV_2O_4 or the perovskite $Gd_{1-x}Sr_xTiO_3$ at the metal-to-insulator transition (MIT) close to $x = 0.2$ [5,6]. In these compounds not only the Kondo effect but also electronic correlations due to frustration or due to the Mott-Hubbard MIT have been suggested to be responsible for the mass enhancement. A brief review can be found in Ref. [7].

In this review, typical heavy-fermion effects on the magnetic resonance properties are illustrated: With respect to usual metals, a strongly enhanced linear increase of the electron spin resonance (ESR) linewidth of appropriate probe spins as well as of the nuclear magnetic resonance (NMR) spin-lattice relaxation rate is observed on increasing temperature T for $T < T^*$.

†This paper is originally written by authors on the occasion of eightieth birthday of Professor Boris I. Kochelaev.

To higher temperatures an intermediate regime governed by spin fluctuations finally transforms into the usual linear Korringa relaxation with moderate slope. While NMR is measured on appropriate nuclei like Cu, Al, Si, or Pt, the ESR signal of the Kondo ion itself is usually not detectable, because the linewidth is of the order of the characteristic temperature and, hence, by far larger than the conventional ESR frequencies of 9 or 35 GHz. An exception are systems with strong ferromagnetic correlations like $YbRh_2Si_2$ or CeRuPO [8, 9]. Thus, usually small amounts of an appropriate ESR probe have to be doped into the compound of interest. In $4f$ or $5f$ derived compounds this is often Gd^{3+} with electron configuration $4f^7$, i.e., a half-filled $4f$ shell and stable spin-only $S = 7/2$ state [10]. Due to vanishing orbital momentum the direct spin-lattice relaxation is negligible and the relaxation via the conduction electrons becomes dominant. The power of Gd^{3+}-ESR to help elucidating the heavy-fermion state in canonical correlated electron systems has been demonstrated, e.g., in Refs. [11–13].

Here we focus on perovskite-related $LaCu_3Ru_4O_{12}$ [14], which exhibits very similar electronic properties like isostructural $CaCu_3Ru_4O_{12}$, in spite of different electronic filling due to trivalent La instead of divalent Ca [15]. With a Sommerfeld coefficient $\gamma = 85$ mJ mol^{-1} K^{-2} per formula unit derived from the specific heat, $CaCu_3Ru_4O_{12}$ is a moderately mass enhanced Fermi liquid showing intermediate valence properties above 2 K, but reveals non-Fermi-liquid behavior for lower temperatures [16–18]. For $LaCu_3Ru_4O_{12}$ on the other hand, low-temperature specific-heat measurements revealed a Sommerfeld coefficient of 139 mJ mol^{-1} K^{-2} per formula unit, indicating a comparable moderate heavy-fermion behavior [15]. In $LaCu_3Ru_xTi_{4-x}O_{12}$ the substitution of Ru by non-magnetic Ti^{4+} ($3d^0$) reduces the mass enhancement as documented from heat-capacity data and a metal-to-insulator transition (MIT) was expected when roughly half of the ruthenium ions is replaced by titanium [15]. However, the exact concentration x_c of the MIT is masked due to a breakdown of the Fermi-liquid behavior in the resistivity for $x < 3$ and Schottky-like anomalies in the specific heat. For $x \leq 2$ a spin-glass phase shows up at low temperatures, which finally transforms into an antiferromagnetically ordered ground state for $x < 0.5$. The question, whether the onset of the spin-glass phase correlates with the MIT, could not be answered on the basis of resistivity and specific-heat measurements so far.

Therefore, electron-spin resonance (ESR) experiments were carried out to investigate in detail the local magnetic properties of the copper and ruthenium ions. Unfortunately, the spin-moment of Ru relaxes by far too fast to yield a well measurable ESR signal. Furthermore, the copper-spin moment also becomes covered by this effect and Cu-ESR is only observable for $x = 0$ [19]. Thus, we doped small amounts of Gd^{3+} as ESR probe on the La site. This enabled us to access locally the electronic properties of $LaCu_3Ru_4O_{12}$ and the MIT induced by Ti substitution.

2. Experimental Details

Polycrystalline samples of $La_{1-y}Gd_yCu_3Ru_xTi_{4-x}O_{12}$ were synthesized for $1 \leq x \leq 4$ by solid-state reaction from the binary oxides La_2O_3 (Chempur, 99.9%), Gd_2O_3 (Aldrich, 99.9%), RuO_2 (Chempur, 99.9%), TiO_2 (Aldrich, 99.9%), and CuO (HelmAG, 99.5%) mixed in appropriate molar amounts. Before synthesis, La_2O_3, Gd_2O_3, and RuO_2 were dried for 6 hours at 900°C in a box furnace. The starting compounds were powdered in an agate mortar with isopropanol. After drying the mixture was pelletized and calcined for 48 hours at 1040°C in a muffle furnace. Excess CuO was added as a flux and removed after the reaction using diluted hydrochloric acid according to Ref. [20]. X-ray diffraction (performed in a *Seifert* TT 3003 diffractometer using Cu $K_{\alpha 1,\alpha 2}$ radiation) proves the proper perovskite derived cubic structure $A'A''_3B_4O_{12}$, space group $Im\overline{3}$ (No. 204), of the samples as exemplarily illustrated in Fig. 1 for the sample with

$x = 3.5$ and $y = 0.05$. In this structure La and Cu occupy the sites A' and A'', respectively, whereas Ru and Ti statistically share the B site [21]. The corresponding Rietfeld refinement has been performed with the program *FullProf Suite* [22].

The concentration dependence of the lattice parameters for all samples under consideration is depicted in Fig. 2. The main frame proves that 5% of gadolinium do not change the cubic lattice parameter a significantly: The cell parameter a increases approximately linearly with ruthenium concentration x, while the changes due to the gadolinium doping remain within experimental uncertainties (±3 mÅ). This is further evident from the inset, which illustrates that only for $y = 0.15$ a small reduction of the lattice parameter of the order of 0.05% can be recognized.

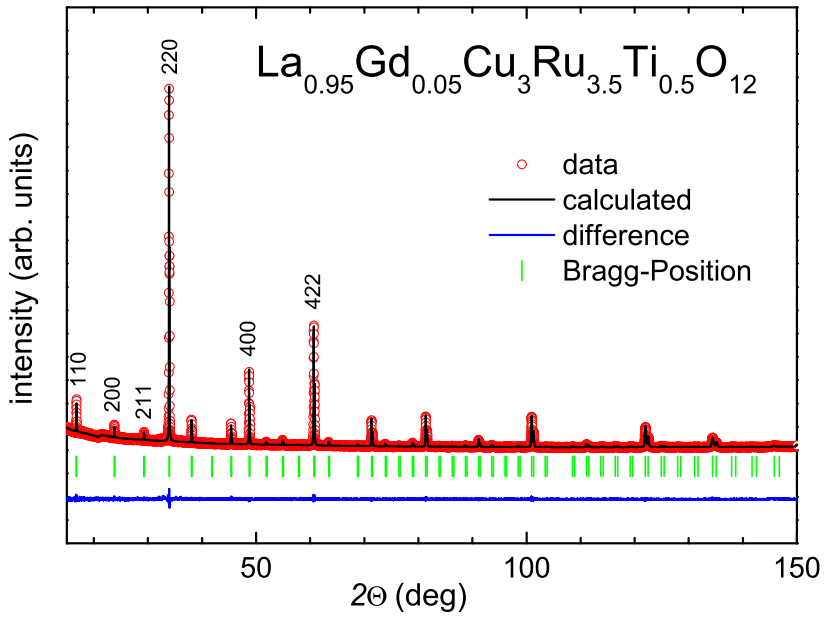

Figure 1. (Color online) Exemplary x-ray diffraction pattern of $La_{0.95}Gd_{0.05}Cu_3Ru_{3.5}Ti_{0.5}O_{12}$ and result of Rietfeld refinement.

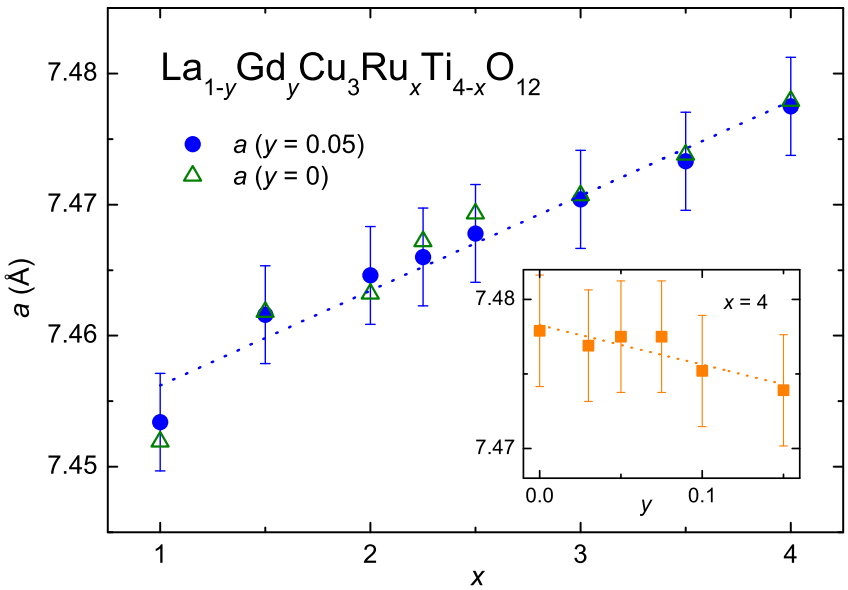

Figure 2. (Color online) Dependence of the cubic lattice parameter a in $La_{1-y}Gd_yCu_3Ru_xTi_{4-x}O_{12}$ on the Ru concentration x in the regime $1 \leq x \leq 4$ for $y = 0$ and $y = 0.05$. Inset: Dependence of a on the Gd concentration y for $x = 4$.

The magnetic susceptibility was investigated using a commercial SQUID magnetometer (*Quantum Design* MPMS5) for temperatures $2 \leq T \leq 400$ K. It turned out that the temperature dependence of the susceptibilities could be well described by the sum of independent contributions of undoped $LaCu_3Ru_xTi_{4-x}O_{12}$ and of the Gd spins. This indicates that the influence of the Gd spins on the basic properties of the undoped compounds is of minor importance. Thus, Gd is well suited to probe the electronic properties of $LaCu_3Ru_xTi_{4-x}O_{12}$ without disturbing them.

The ESR experiments have been performed at X-band frequency ($\nu \approx 9.4$ GHz) in a *Bruker* ELEXSYS E500 continuous-wave spectrometer. For cooling an *Oxford Instruments* ESR 900 continuous He-gas flow cryostat was used providing temperatures $4.2 \leq T \leq 300$ K. Because of the applied Lock-In technique with field modulation, the ESR spectra record the field derivative dP_{abs}/dH of the microwave power absorbed by the sample due to induced magnetic dipolar transitions between the Zeeman levels of the probe spins as a function of the static external magnetic field H.

3. Results

Fig. 3 depicts characteristic Gd^{3+}-ESR spectra taken in $La_{0.95}Gd_{0.05}Cu_3Ru_xTi_{4-x}O_{12}$. The spectrum of $x = 4$ is characteristic for the metallic regime. The asymmetric single exchange-narrowed line is well described in terms of a Dyson-type shape, i.e. an asymmetric Lorentz line which contains a certain contribution $0 \leq \alpha \leq 1$ of dispersion besides the usual absorption because of the skin effect arising from the conductivity [23, 24]. Moreover, due to the large linewidth ΔH observed at elevated temperatures, the counter resonance at negative resonance field $-H_{\mathrm{res}}$ had to be taken into account when fitting the ESR spectra [25]. In comparison to $x = 4$ with $\alpha = 0.78$ the spectrum becomes nearly symmetric ($\alpha \to 0$) on decreasing x, resulting from decreasing conductivity on approaching the metal-to-insulator transition. At the same time deviations from the ideal Lorentz shape become significant for $x \leq 2$ and the fit is poor for $x = 1.5$. This indicates the breakdown of the exchange narrowing in the insulating regime, i.e. because of the lack of conduction electrons. Thus, already from the ESR line shape we are able to localize the MIT close to $x = 2$.

Before going into details of the MIT, we decribe the influence of the Gd concentration y on the ESR properties of $La_{1-y}Gd_yCu_3Ru_4O_{12}$. Fig. 4 shows the temperature dependence of the resonance linewidth ΔH for different Gd concentrations $0.05 \leq y \leq 0.15$. For all samples we recognize a steep linear increase of the linewidth with temperature with a slope of about 24 Oe/K up to about 50 K. For higher temperatures $\Delta H(T)$ exhibits a negative curvature. The data for $y > 0.075$ exhibit a significantly increasing residual linewidth ΔH_0 indicating the influence of disorder or non-zero contribution of the Gd-Gd interactions. It has to be noted, however, that the g value of $La_{1-y}Gd_yCu_3Ru_4O_{12}$ is practically independent on the Gd concentration at $g = 1.89$.

Nevertheless, to be sure that the Gd-Gd interaction does not influence the results, we performed all ESR investigations of the Ti:Ru substitutional series using a Gd concentration $y = 0.05$. Fig. 5 shows the temperature dependence of linewidth (main frame) and g value (inset) for $2 \leq x \leq 4$. For lower Ru contents the evaluation with a single exchange-narrowed line is not reasonable any more. With decreasing Ru content one recognizes a significant increase of the residual linewidth. All data sets intersect each other close to 35 K and exhibit qualitatively a similar temperature dependence with a clearly linear increase below 50 K followed by a weaker linear increase at elevated temperatures. Only the absolute slope systematically decreases with

decreasing x on approaching $x = 2$. The g values are only weakly temperature dependent and gradually increase with decreasing x from $g(x = 4) \approx 1.89(1)$ approaching $g(x = 2) \approx 1.99(1)$.

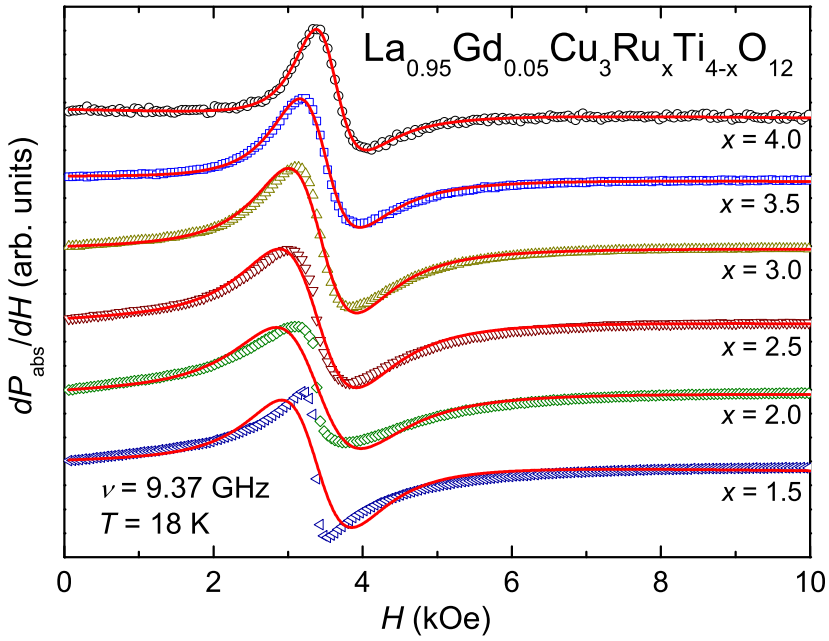

Figure 3. (Color online) Typical ESR signals for $La_{0.95}Gd_{0.05}Cu_3Ru_xTi_{4-x}O_{12}$ with different Ru content x. The red solid lines indicate the fits by a Dyson-type shape as described in the text. Deviations show up for $x \leq 2$ indicating the insulating regime where the exchange-narrowing process by conduction electrons drops out.

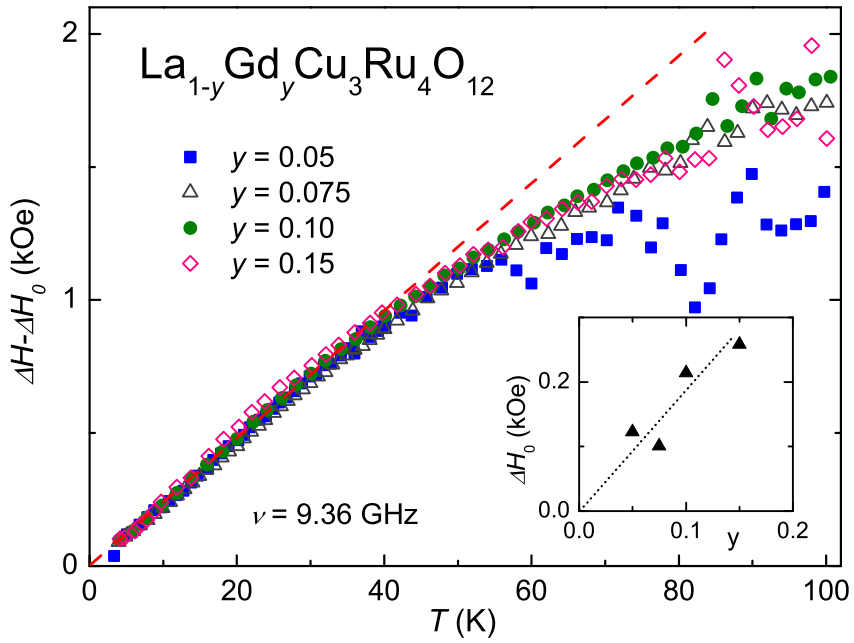

Figure 4. (Color online) Temperature dependence of the resonance linewidth ΔH after subtraction of the residual linewidth ΔH_0 for $La_{1-y}Gd_yCu_3Ru_4O_{12}$ with different Gd concentration $0.05 \leq y \leq 0.15$. The dashed line indicates the linear Korringa regime at low temperatures due to enhanced effective electronic masses. Inset: Dependence of the residual linewidth on y.

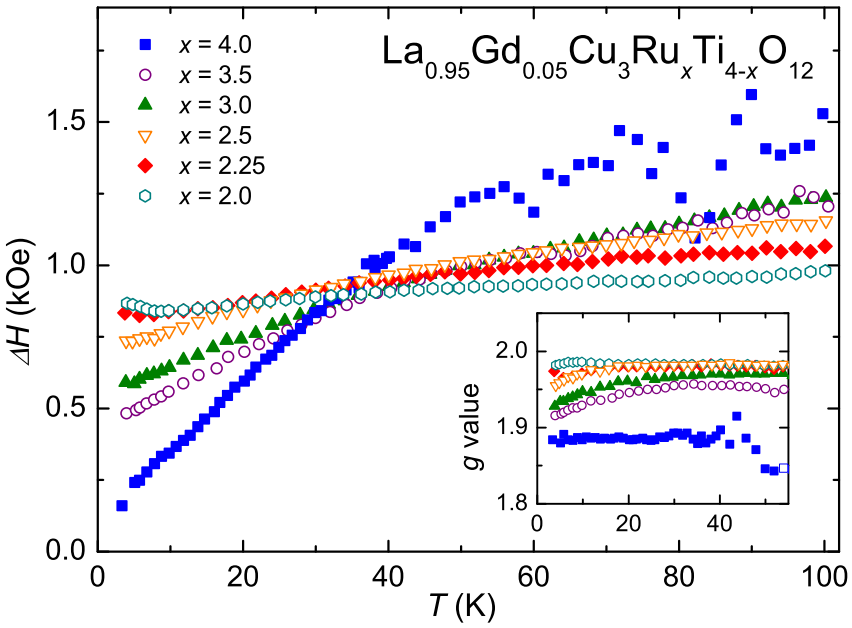

Figure 5. (Color online) Temperature dependence of the resonance linewidth ΔH for $La_{0.95}Gd_{0.05}Cu_3Ru_xTi_{4-x}O_{12}$ for $2 \leq x \leq 4$. Inset: Temperature dependence of the corresponding g values.

4. Discussion

The observed properties of the resonance linewidth in $La_{1-y}Gd_yCu_3Ru_4O_{12}$ are characteristic for heavy-fermion compounds. NMR measurements on ^{101}Ru and ^{63}Cu in the related compound $CaCu_3Ru_4O_{12}$ have shown that at low temperatures the effective electronic masses are strongly enhanced on the Ru site, but turn out to become even reduced at the Cu site [18]. Thus, compared to the canonical $4f$-electron based heavy-fermion compounds like $CeCu_2Si_2$ or $CeAl_3$, ruthenium plays the role of the $4f$-Kondo ion, which is screened by the conduction electrons. Hence, following Ref. [26] the ESR linewidth consists of two contributions, i.e. one due to the direct exchange of the Gd spin with the conduction electrons and the second due to the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange with the fluctuating Ru spins transferred by the conduction electrons. This can be expressed by:

$$\Delta H - \Delta H_0 = \Delta H_{\rm ce} + \Delta H_{\rm Ru} = b_{\rm K} T + A_{\rm RKKY} T \tau \chi_{\rm Ru} \qquad (1)$$

where ΔH_0 contains all temperature independent contributions due to disorder or impurities. The first term is the usual Korringa relaxation linear in temperature T with the slope $b_{\rm K} \propto \langle J^2(q) \rangle N^2(E_{\rm F})$ determined by the electronic density of states $N(E_{\rm F})$ at the Fermi energy $E_{\rm F}$ and the exchange integral J averaged over all possible momentum transfers q. The second term depends on the fluctuation time τ of the Ru spins and on their static susceptibility $\chi_{\rm Ru}$. The prefactor $A_{\rm RKKY}$ averages over the squared RKKY exchange integrals. In canonical heavy-fermion compounds for temperatures far below the characteristic temperature T^*, the spin fluctuation time is approximately temperature independent $\tau(T) \propto 1/T^*$ and the susceptibility is Pauli-like but strongly enhanced with respect to usual metals. This results in an enhanced Korringa-like linear increase of the linewidth for $T \ll T^*$. For elevated temperatures $T \gtrsim T^*$ the fluctuations become faster $\tau(T) \propto T^{-1/2}$ following Ref. [27]. The susceptibility decreases with a Curie-Weiss law $\propto (T - \Theta)^{-1}$. Thus, the heavy-fermion contribution becomes gradually suppressed, providing the bare Korringa relaxation via the conduction electrons at high temperatures.

In Gd doped $LaCu_3Ru_4O_{12}$ a characteristic temperature of about $T^* \approx 50$ K separates the linear Korringa-like low-temperature regime with an enhanced slope of $b_L \approx 24$ Oe/K from the high-temperature regime with an asymptotic Korringa slope of $b_H \approx 7$ Oe/K. This enhancement by a factor of about 3 is significantly weaker than the factor of 40 obtained from ^{101}Ru-NMR in $CaCu_3Ru_4O_{12}$. This can be explained by the fact that the ESR probe feels the enhancement only via the RKKY interaction which decreases $\propto 1/R^6$ with the distance R of the ESR probe from the Ru ions, while NMR measures in that case directly at the Ru ions where the heavy fermion masses are formed [12].

Similar to the linewidth we can consider the g value to contain contributions from the Pauli susceptibility of the conduction electrons $\Delta g_{ce} \propto J(0)N(E_F)$ as well as from the local moments of the Ru ions $\Delta g_{Ru} \propto \chi_{Ru}$ mapping the local susceptibility analogously to the Knight shift in NMR. Indeed, Gd doped $LaCu_3Ru_4O_{12}$ exhibits a significant negative g shift $\Delta g = g - g_{ins} \approx -0.1$ from its insulator value $g_{ins} = 1.993$ [28]. Compared to usual metals this seems to be surprising, because the uniform magnetic polarization of the conduction electrons in the external field usually gives rise to an additional internal magnetic field supporting the external field and, therefore, to a positive g shift. However, the exchange geometry including d electrons sometimes can reverse the sign as reported earlier in Gd-doped Laves phases [10] and also recently in iron pnictides [29]. The quite large absolute value of the g shift corroborates the heavy-fermion properties of $LaCu_3Ru_4O_{12}$.

On substitution of ruthenium by titanium the characteristic heavy-fermion type contribution to the linewidth remains discernible but becomes gradually suppressed down to $x = 2$. Although the characteristic temperature derived from the kink at $T^* \approx 50$ K is not changed, the absolute value of this relaxation contribution strongly decreases on decreasing Ru content x while only the temperature independent residual linewidth increases. At the same time the g value progressively approaches the insulator value. This behavior strongly reminds of the situation in the canonical heavy-fermion compound $Y_{1-x}Ce_xAl_2$, where the magnetic Ce^{3+} (electronic configuration $4f^1$) Kondo ion is gradually replaced by non magnetic Y^{3+} ions. In that compound Gd-ESR was applied to characterize the transformation from the concentrated Kondo lattice to diluted Kondo ions [26]. Indeed, those experiments revealed the local character of the Kondo effect even in the concentrated heavy-fermion lattice, because the linewidth can be understood just as the sum of independent contributions of Ce^{3+} spin fluctuations and conduction electrons, where the strength of the former is just proportional to the concentration x of the cerium ions with only slightly varying characteristic temperature $T^* \approx 10$ K.

The main difference between $Y_{1-x}Ce_xAl_2$ and $LaCu_3Ru_xTi_{4-x}O_{12}$ is the fact that the former compound is a metal in the whole concentration range, while the latter undergoes a metal-to-insulator transition, which from electrical resistivity measurements could only roughly be localized in the range $2 \leq x \leq 3$ [21]. This means that on decreasing Ru content, not only the contribution due to Ru spin fluctuations but also the direct Korringa relaxation is switched off as the MIT takes place. Therefore, to identify the MIT, Fig. 6 depicts the dependence of both the low-temperature slope b_L and the high-temperature slope b_H on the Ru content x, characterizing the contributions of Ru spin fluctuations as well as the direct Korringa relaxtion, respectively. As expected, the relaxation due to Ru spin fluctuations monotonously decreases on decreasing Ru content x, while the direct Korringa contribution decreases only slightly until it drops to $b_H < 1$ Oe/K at $x = 2.25$.

Thus, the MIT in $LaCu_3Ru_xTi_{4-x}O_{12}$ is characterized just by fading of the metallic relaxation contributions without any critical divergence. This is in contrast to the behavior observed

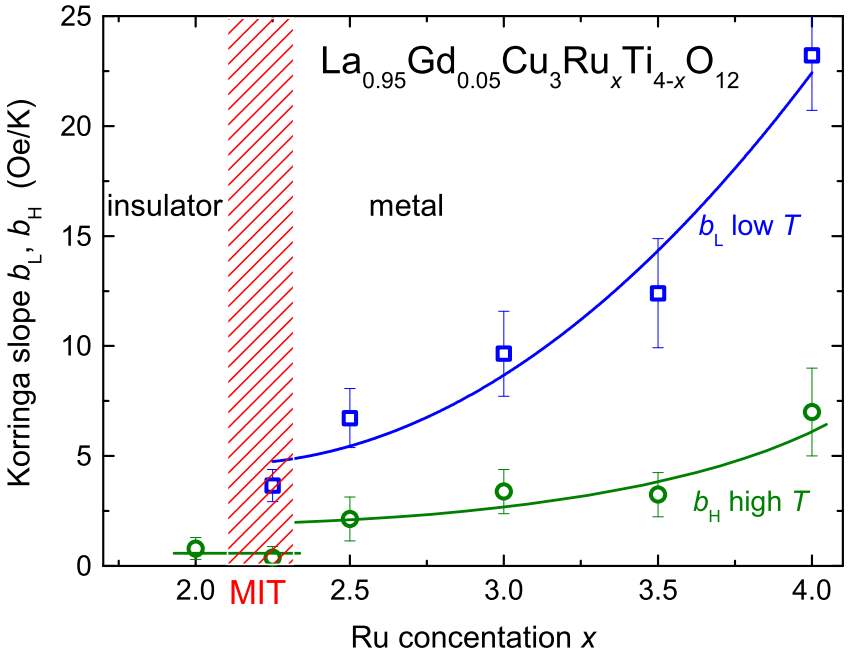

Figure 6. (Color online) Korringa slope b_{L} and b_{H} determined from the temperature dependence of the ESR linewidth below and above 50 K, respectively, as a function of the Ru content x for $La_{0.95}Gd_{0.05}Cu_3Ru_xTi_{4-x}O_{12}$.

for example in $Gd_{1-x}SrTiO_3$ [6]. where the heavy-fermion type relaxation contribution diverges on approaching the MIT from the metallic regime due to diverging effective electronic masses as also documented by specific-heat measurements on the related compounds $La_{1-x}Sr_xTiO_3$ and $Y_{1-x}Ca_xTiO_3$ [30, 31]. The basic difference is that in those compounds the substitution does not replace the Ti ions themselves but only changes the electronic filling on the Ti sites between $3d^0$ ($x = 1$, Ti^{4+}) and $3d^1$ ($x = 0$, Ti^{3+}). The $3d$ electrons can move on the Ti lattice and the correlations increase with increasing number of $3d$ electrons, giving rise to enhancing effective masses and finally to the formation of the Mott insulator.

In contrast, in $LaCu_3Ru_xTi_{4-x}O_{12}$, the magnetic Ru^{4+} ions (electronic configuration $4d^4$ determined from XANES) [21], at which the heavy-fermion formation takes place, are substituted by nonmagnetic Ti^{4+} ions with empty $3d$ shells. Therefore, Ti substitution breaks the lattice periodicity of the heavy-fermion system and strongly disturbs the $4d$ band structure. This in turn inhibits the conductivity, while the electronic filling remains unaffected by the substitution. Note also that regarding previous NMR measurements in $CaCu_3Ru_4O_{12}$, electronic mass enhancement is not expected at the copper site. Thus, as soon as approximately 50% of the Ru ions are replaced by Ti ions, practically all Cu-$3d$ electrons are randomly localized at the Cu ions giving rise to the insulating state and spin-glass phase at low temperatures.

5. Conclusion

The present investigations clearly show that electron spin resonance as a local probe is able to access electronic properties in a solid, which are otherwise difficult or even impossible to obtain by means of bulk methods like electrical resistivity of specific-heat measurements. In $LaCu_3Ru_xTi_{4-x}O_{12}$ the conductivity is strongly affected by local moment scattering leading to an increasing resistivity with decreasing temperature for $x \leq 3$ in the metallic regime. At the same time the specific heat is governed by the corresponding Schottky anomalies. Therefore,

only the spin relaxation of the ESR probe Gd allowed determining the evolution of the electronic ground state, which changes from a heavy-fermion metal at $x > 2.25$ into a semiconductor or insulator with spin-glass ground state for lower Ru content $x \leq 2$. Thus, the Ru concentration of the metal-to-insulator transition can be approximately localized at $x_c \approx 2.25$

Acknowledgments

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